Supporting Information

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Metallacarborane-Based Nanostructures:

A Carbon-Wired Planar Octagon**

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Synthesis of 3 from 1a: To a solution of 73 mg of trimethylsilylacetylene (0.75 mmol) in 4 mL of THF was added 0.5 mL of 1.51 M solution of *n*-BuLi in hexane (0.75 mmol) at 0°C. After stirring 0.5 h, 102 mg (0.75 mmol) of anhydrous ZnCl₂ in 2 mL of THF was added at 0°C and the mixture was stirred at room temperature for 2 h. 100 mg (0.25 mmol) of Cp*Co(2,3-Et₂C₂B₄H₃-7-Br)² and 14 mg (0.013 mmol) of Pd(PPh₃)₄ were added and the mixture was refluxed for 4.5 days, after which the solvent was removed in vacuo and flash chromatographed through 3cm of silica gel in 50% 1:1 hexane:CH₂Cl₂ to give one orange band. Removal of solvent gave 85 mg of orange red product (81%).

Data for 3: ¹H NMR (300 MHz, CDCl₃): δ = -0.04 (s, 9H, SiMe₃), 1.35 (t, 6H, *J* = 7.5 Hz, ethyl CH₃), 1.77 (s, 15H, C₅Me₅), 2.30, 2.46 (sextet, 2H, *J* = 7.5 Hz, ethyl CH₂). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ = -0.4 (SiMe₃), 10.0 (C₅Me₅), 14.3 (ethyl CH₃), 22.0 (ethyl CH₂), 90.9 (C₅Me₅), 92.0 (C≡CSiMe₃), 93.4 (C₂B₄). ¹¹B NMR (96.4 MHz, CDCl₃): δ = -3.9 (s, 1B), 3.7 (d, 2B, unresolved), 11.9 (d, 1B, unresolved). IR (KBr pellet, cm⁻¹): ν = 2969.4 (vs), 2931.8 (s), 2872.4 (m), 2522.1 (vs, B-H), 2126.1 (w, C≡C), 1472.0 (m), 1452.2 (m), 1377.2 (s), 1247.4 (s), 1168.4 (w), 1140.9 (s), 1111.3 (m), 1062.8 (m), 1026.7 (m), 857.8 (vs), 814.0 (vs), 760.1 (m), 696.8 (w). CI⁺-mass: *m/z* (%) = 420.4 ([M⁺], 100).

Synthesis of $\text{C}_6\text{H}_4\text{O}_2\text{BC}\equiv\text{CSi}(\text{CH}_3)_3$: To a solution of 5.50 g of $(\text{CH}_3)_3\text{SiC}\equiv\text{CSnMe}_3^1$ (21.07 mmol) in 40 mL of toluene, 3.3 g of $\text{C}_6\text{H}_4\text{O}_2\text{BCl}$ (21.4 mmol) in 80 mL of toluene was added at -78°C . The mixture was allowed to warm to room temperature over 7 hours, and stirred for a further 12 hours. The solvent was removed in vacuo to give light yellow liquid. The product was purified by distillation (62°C , 0.12 torr) to give a colorless liquid (3.9 g, 86%). ^1H NMR (300 MHz, CDCl_3): δ = 0.28 (s, 9H, SiMe_3), 7.11-7.14 (m, 2H, C_6H_4), 7.23-7.26 (m, 2H, C_6H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3): δ = -0.7 ($\text{Si}(\text{CH}_3)_3$), 65.9 ($\text{C}\equiv\text{C}$), 112.5 (C_6H_4), 123.1 (C_6H_4), 147.5 (C_6H_4). ^{11}B NMR (96.4 MHz, CDCl_3): δ = 23.1 (s). CI^+ -mass: m/z (%) = 216.0 ($[\text{M}^+]$, 100).

Synthesis of 3 from 2: A solution containing 632 mg (2.01 mmol) of $\text{Cp}^*\text{CoEt}_2\text{C}_2\text{B}_3\text{H}_5$ (**2**) in 40 mL toluene at 0°C was treated with 2.5 mL (4.02 mmol) of 1.65 M *tert*-butyllithium. The solution turned dark red orange as it was warmed to room temperature, the stirring continued for over 6 hours. The mixture was cooled to 0°C and $\text{C}_6\text{H}_4\text{O}_2\text{BCCSi}(\text{CH}_3)_3$ (0.97 g, 4.49 mmol) in 10 mL toluene was added at 0°C . The mixture was allowed to warm to room temperature, and stirred for a further 24 hours, after which the toluene was removed in vacuo. The residue was taken up in CH_2Cl_2 and washed through 3 cm of silica with CH_2Cl_2 . The CH_2Cl_2 wash was column-chromatographed on silica in hexane to recover 62 mg starting material, which was eluted in 50% 1:1 CH_2Cl_2 :hexane to afford 615 mg of pure **3** as an orange red, air-stable crystalline solid (72.9% yield, 80.7% based on the starting complex consumed).

Data for 4: ^1H NMR (300 MHz, CDCl_3): δ = -0.01 (s, 9H, SiMe_3), 1.33 (t, 6H, J = 7.5 Hz, ethyl CH_3), 1.77 (s, 15H, C_5Me_5), 2.31, 2.47 (sextet, 2H, J = 7.5 Hz, ethyl CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ = -0.5 (SiMe_3), 9.6 (C_5Me_5), 14.4 (ethyl CH_3), 21.7 (ethyl CH_2), 91.7 (C_5Me_5), 92.1 ($\text{C}\equiv\text{C}$), 95.4 (C_2B_4). ^{11}B NMR (96.4 MHz, CDCl_3): δ = -5.0 (s, 1B), 4.0 (BH, 3B, unresolved). IR (KBr pellet, cm^{-1}): ν = 2971.3 (vs), 2932.9 (s), 2911.4 (m), 2873.1 (m), 2545.4 (s, B-H), 2126.3 (w, $\text{C}\equiv\text{C}$), 1456.8 (m), 1422.9 (m), 1382.7 (s), 1259.2 (m), 1247.6

(s), 1182.5 (m), 1151.5 (s), 1116.8 (m), 1065.5 (m), 1025.6 (s), 852.6 (vs), 785.1 (s), 698.3 (m), 618.3 (m). CI^+ -mass: m/z (%) = 547.2 ($[\text{M}^+]+1$, 100).

Data for 5: ^1H NMR (300 MHz, CDCl_3): δ = 1.34 (t, 6H, J = 7.5 Hz, ethyl CH_3), 1.74 (s, 1 h, $\text{C}\equiv\text{CH}$), 1.78 (s, 15H, C_5Me_5), 2.30, 2.47 (sextet, 2H, J = 7.5 Hz, ethyl CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ = 9.6 (C_5Me_5), 14.4 (ethyl CH_3), 21.5 (ethyl CH_2), 78.0 ($\text{C}\equiv\text{C}$), 91.8 (C_5Me_5), 91.9 ($\text{C}\equiv\text{C}$), 94.9 (C_2B_4). ^{11}B NMR (96.4 MHz, CDCl_3): δ = -5.4 (s, 1B), 4.2 (BH, 3B, unresolved). IR (KBr pellet, cm^{-1}): ν = 3267.9 (vs, $\text{C}\equiv\text{CH}$), 2970.8 (m), 2933.6 (m), 2873.3 (w), 2534.9 (s, B-H), 2060.6 (m, $\text{C}\equiv\text{C}$), 1457.0 (m), 1452.2 (m), 1378.4 (vs), 1019.5 (m), 808.0 (s), 679.2 (s), 671.8 (s), 668.2 (s). CI^+ -mass: m/z (%) = 475.3 ($[\text{M}^+]+1$, 100).

Data for 6: ^1H NMR (300 MHz, CDCl_3): δ = 0.22 (s, 9H, $\text{BC}\equiv\text{CSiMe}_3$), 1.33 (t, 6H, J = 7.5 Hz, ethyl CH_3), 1.65 (s, 1 h, $\text{C}\equiv\text{CH}$), 1.80 (s, 15H, C_5Me_5), 2.26, 2.43 (sextet, 2H, J = 7.5 Hz, ethyl CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3): δ = 0.4 ($\text{BC}\equiv\text{CSiMe}_3$), 9.3 (C_5Me_5), 14.4 (ethyl CH_3), 21.7 (ethyl CH_2), 77.3 ($\text{BC}\equiv\text{CH}$), 91.2 (C_5Me_5), 94.3 (C_2B_4), 116.0 ($\text{BC}\equiv\text{CSiMe}_3$). ^{11}B NMR (96.4 MHz, CDCl_3): δ = -4.8 (s, 1B), 3.9 (d, 2B, broad), 8.0 (s, 1B). IR (KBr pellet, cm^{-1}): ν = 3260.0 ($\text{C}\equiv\text{CH}$), 2963.6 (s), 2910.8 (s), 2558.5 (s, B-H), 2106.8 (s, $\text{C}\equiv\text{C}$), 2060.3 (s, $\text{C}\equiv\text{C}$), 1476.4 (m), 1448.4 (m), 1378.6 (m), 1244.6 (s), 1189.4 (m), 1058.5 (m), 1022.6 (m), 892.6 (s), 837.4 (vs), 813.5 (s), 759.2 (s), 697.1 (s), 679.9 (s). UV-vis (CH_2Cl_2 , nm (%)): 304 (100), 229 (46), 262 (16) $\epsilon_{\text{max}} = 38,200 \text{ cm}^{-1} \text{ M}^{-1}$. CI^+ -mass: m/z (%) = 445.5 ($[\text{M}^+]+1$, 100).

Synthesis of 7: To a mixture of 300 mg (0.634 mmol) $\text{Cp}^*\text{Co}(2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_2\text{-5-I-7-C}\equiv\text{CH})$, 10 mg (0.014 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 6 mg (0.031 mmol) of cupric chloride, 80 mg (0.317 mmol) of I_2 , 6 ml of Pyridine and 1 ml of Et_3N were added. The mixture was stirred at room temperature for 3 h. Solvent was removed in vacuo and flash chromatographed through 3cm of silica gel in CH_2Cl_2 . CH_2Cl_2 wash was column chromatographed (15 cm) on silica gel and eluted with a 2.1

CH₂Cl₂/hexane to afford 210 mg of pure product as a red solid. (70% yield).

Data for 7: ¹H NMR (300 MHz, CDCl₃): δ = 1.25 (t, 12H, *J* = 8 Hz, ethyl CH₃), 1.73 (s, 30H, C₅Me₅), 2.20, 2.38 (sextet, 4H, *J* = 8Hz, ethyl CH₂). ¹³C NMR (75.4 MHz, CDCl₃): δ = 9.6 (C₅Me₅), 14.7 (ethyl CH₃), 21.5 (ethyl CH₂), 74.8 (C≡C), 91.8 (C₅Me₅), 92.0 (C≡C), 95.8 (C₂B₄). ¹¹B NMR (96.4 MHz, CDCl₃): δ = -5.8 (s, 2B), 4.2 (BH, 4B, unresolved). IR (KBr pellet, cm⁻¹) ν = 2971.9 (s), 2922.4 (s), 2873.0 (m), 2549.3 (vs, B-H), 2092.2 (m, C≡C), 1472.0 (m), 1465.1 (m), 1457.0 (m), 1448.2 (m), 1383.1 (s), 1376.9 (s), 1137.3 (m), 1109.5 (m), 1022.4 (s), 840.3 (w), 803.7 (s), 641.8 (w), 521.2 (w). CI⁺-mass: m/z (%) = 946.0 ([M⁺], 100).

Synthesis of 8 from 7: Trimethylsilylacetylene (65.4 mg, 0.67 mmol) was deprotonated with 0.44 ml (0.67 mmol) of a 1.51M *n*-butyllithium solution in hexane in 8 ml THF. After stirring 0.5 h, 91 mg (0.67 mmol) of anhydrous ZnCl₂ in 10 ml of THF was added at 0°C. The mixture was stirred at room temperature for 2 h. Then 210 mg (0.22 mmol) of [Cp*Co(2,3-Et₂C₂B₄H₂-5-I-7-C≡C)]₂ (**7**) and 15 mg (0.013 mmol) of Pd(PPh₃)₄ were added. The mixture was refluxed for 3.5 days, after which the solvent was removed in vacuo and flash chromatographed through 5 cm of silica gel in 1:1 Hexane/CH₂Cl₂ to give one orange band. Removal of solvent gave orange red product (177mg, 91%).

Data for 8: ¹H NMR (300 MHz, CDCl₃): δ = 0.20 (s, 18H, BC≡CSiMe₃), 1.24 (t, 12H, *J* = 7.8 Hz, ethyl CH₃), 1.76 (s, 30H, C₅Me₅), 2.18, 2.35 (sextet, 4H, *J* = 7.8 Hz, ethyl CH₂). ¹³C NMR (75.5 MHz, CDCl₃): δ = 0.5 (BC≡CSiMe₃), 9.4 (C₅Me₅), 4.6 (ethyl CH₃), 21.7 (ethyl CH₂), 74.5 (BC≡C-C≡CB), 91.2 (C₅Me₅), 95.2 (C₂B₄), 116.2 (BC≡CSiMe₃). ¹¹B NMR (96.4 MHz, CDCl₃): δ = -5.0 (s, 2B), 4.1 (BH, 4B, unresolved), 7.8 (s, 2B). IR (KBr pellet, cm⁻¹): ν = 2967.7 (s), 2933.8 (m), 2910.1 (m), 2550.0 (s, B-H), 2197.4 (m, C≡C), 1475.2 (w), 1453.0 (w), 1382.9 (m), 1254.1 (s), 1183.0 (w), 1103.9 (m), 1057.5 (m),

896.7 (w), 854.6 (vs), 838.7 (vs), 757.5 (m, 698.3 (w). UV-vis (CH_2Cl_2 , nm (%)): 323 (100), 230 (43), 265 (22), 281 (16) $\epsilon_{\text{max}} = 103,000 \text{ cm}^{-1} \text{ M}^{-1}$. CI^+ -mass: m/z (%) = 742.6 ($\text{M}^+ - 2 \text{ S SiMe}_3$], 100). 886.5 ($[\text{M}^+]$, 20).

Data for 9: ^1H NMR (300 MHz, CDCl_3): δ = 1.25 (t, 12H, J = 7.5 Hz, ethyl CH_3), 1.77 (s, 30H, C_5Me_5), 2.18, 2.35 (sextet, 4H, J = 7.8 Hz, ethyl CH_2), 3.19 (s, 1 h, $\text{C}\equiv\text{CH}$). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 9.5 (C_5Me_5), 14.6 (ethyl CH_3), 21.7 (ethyl CH_2), 74.5 ($\text{BC}\equiv\text{C}-\text{C}\equiv\text{CB}$), 91.2 (C_5Me_5), 95.1 (C_2B_4), 96.5 ($\text{C}\equiv\text{CH}$). ^{11}B NMR (96.4 MHz, CDCl_3): δ = -4.8 (s, 2B), 4.3 (4B, BH unresolved), 7.6 (s, 2B). IR (KBr pellet, cm^{-1}): ν = 3303.0 (m, $\text{C}\equiv\text{CH}$), 3284.6 (m, $\text{C}\equiv\text{CH}$), 2965.8 (s), 2930.9 (s), 2909.0 (m), 2873.1 (w), 2547.0 (vs, B-H), 2532.5 (vs, B-H), 2084.9 (s, $\text{C}\equiv\text{C}$), 2046.0 (w, $\text{C}\equiv\text{C}$), 1476.4 (m), 1456.9 (m), 1379.8 (s), 1200.3 (w), 170.8 (w), 1101.5 (m), 1071.5 (m), 1054.6 (m), 1023.4 (m), 807.3 (s), 653.7 (s), 592.3 (s). UV-vis (CH_2Cl_2 , nm (%)): 320 (100), 230 (42), 258 (24) $\epsilon_{\text{max}} = 93,100 \text{ cm}^{-1} \text{ M}^{-1}$. CI^+ -mass: m/z (%) = 742.7 ($[\text{M}^+]$, 100).

References:

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